

LA-UR-21-31065

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Title: Polymer Equations of State and Shock-Driven Decomposition

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Intended for: Invited talk at Sandia National Lab, Albuquerque

Issued: 2021-11-12 (rev.1)

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Polymer Equations of State and Shock-Driven Decomposition

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Physics & Chemistry of Materials (T-1)
Los Alamos National Laboratory

November 9, 2021



Managed by Triad National Security, LLC for the U.S. Department of Energy's NNSA

Quick Overview

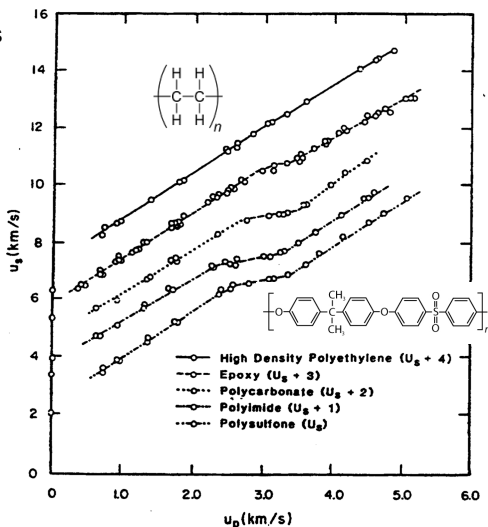
- LANL started taking greater interest in polymer EOS in late 2000's
 - Possible cause of poor simulation results
 - Historically neglected

- Themes that have emerged from that work
 - Polymers decompose chemically when driven at HE detonation pressures
 - Porosity affects decomposition
 - Decomposition affects flow
 - Implications of \uparrow for modeling

Polymer Hugoniots Contain Structure

- Derivative discontinuities at $u_p \sim 3$ km/s ($P \sim 25$ GPa)
- Middle line segment not at equilibrium
- Volume reduction in P - V
 - Degree of reduction correlates qualitatively with chemical structure

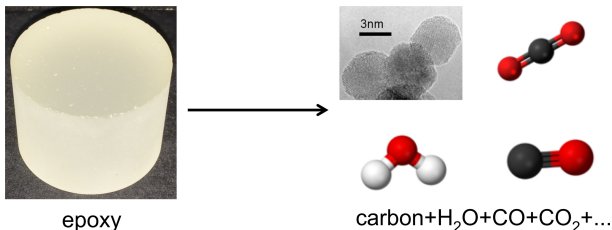
Material name	$P_{\text{threshold}}$ (GPa)	$\Delta V_{\text{tr}}/V(\%)$
epoxy	23.1	3.9
PMMA	26.2	3.4
PTFE	41.6	1.1
PE (linear)	24.7	0.4
polycarbonate	20.0	11.4
phenolic	23.2	6.7
polysulfone	18.5	12.9
polyurethane	21.7	7.3



Carter & Marsh, LA-13006-MS, LANL (originally prepared in 1977)

Hugoniot Structure: Two Early Views

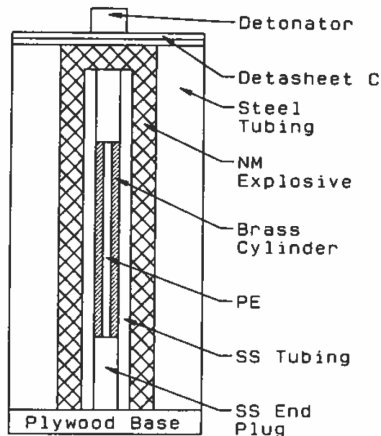
- Phase transition (LANL, 1977)
 - analogous to graphite→diamond
 - “compression...is two-dimensional in nature” below the transition, “more typical of a three-dimensional solid” above
- Decomposition (LLNL, 1979)
 - “..hydrocarbons at high pressure ($\gtrsim 10$ GPa) and high temperature ($\gtrsim 1000$ K) dissociate into carbon in the diamond phase and hydrogen in a condensed molecular phase”



Hugoniot Structure: Recovery Experiments

- Experiments on polyethylene and Teflon
- Setup
 - Single-shock, Mach compression
 - Hermetically-sealed capsule
 - Enabled recovery of soot and gases
 - Mass spectrometry, XRD, TEM
- Polyethylene results
 - Polymer recovered at ~ 20 GPa
 - Gases and soot recovered 28-40 GPa
 - Gases were $>80\%$ mol CH_4 and H_2
 - Soot was neither graphite nor diamond

\Rightarrow different material (with different EOS) when shocked above threshold



PE: *SCCM-1989*, p. 687; PTFE: *J. Chem. Phys.* **80**, 5203 (1984)

Reactant EOS: SESAME Framework

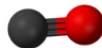
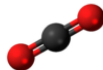
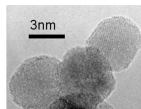
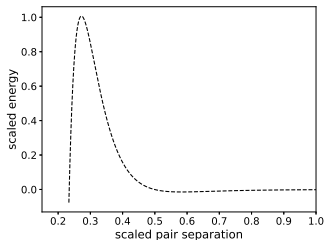
- Purely volumetric, no strength or viscoelasticity
- 3-part decomposition for free energy of each phase

$$F(\rho, T) = \phi(\rho) + F_{\text{ion}}(\rho, T) + F_{\text{elec}}(\rho, T)$$

- Minimize F as function of mass fractions \rightarrow equilibrium phase boundaries
- With regard to polymers:
 - Cold curve extracted from fit to shock data
 - This assumes Mie-Grüneisen form: $P(\rho, E) = P_{\text{ref}}(\rho) + \rho\Gamma(\rho)(E - E_{\text{ref}}(\rho))$
 - Ionic models are generalizations of Debye
 - Polymer thermal response *not* well-described by single Θ
 - Thomas-Fermi-Dirac for electrons
 - Electronic excitations not that important for $\rho_{\text{H}}/\rho_0 \lesssim 3$
 - Typically one phase + liquid
 - Liquid usually pretty hacky

Products EOS: Thermochemical Modeling

- Decomposition products as mixture of fluids and bulk solids
 - Each constituent has its own free energy model
 - Fluids: spherical, pairwise interaction potential (EXP6) translated to free energy with perturbation theory
 - Solids: SESAME model
 - Mixture rule required (non-unique)
- Assume full thermodynamic (and thus, chemical) equilibrium
 - Adjust concentrations until minimal free energy found and stoichiometry preserved

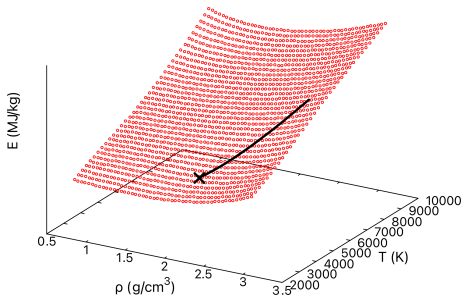


carbon+H₂O+CO+CO₂+...

Leiding, et al., "Reactive Monte Carlo Validation of Thermochemical Equations of State, " *AIP Conf. Proc.* **2272**, 030017 (2020)

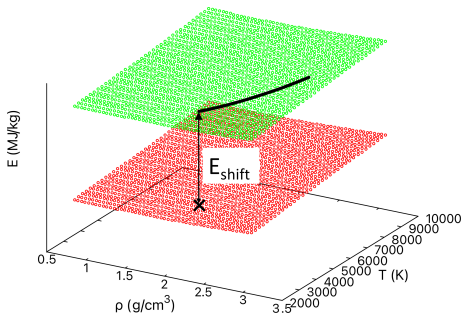
Products EOS: Heat of Reaction

- The origin of a products Hugoniot lies on a separate EOS surface
- Thermochemical EOS surface determined purely by stoichiometry
- Offset from the reactant surface is not
 - closely related to heat of formation
 - essential for capturing energy absorption or release
- We've done this in two ways:
 - adjust to shock data
 - calculate from heat of combustion



Products EOS: Heat of Reaction

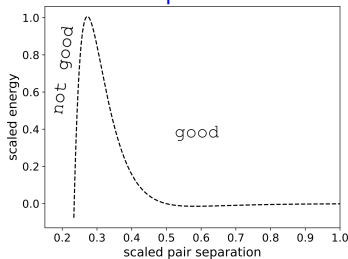
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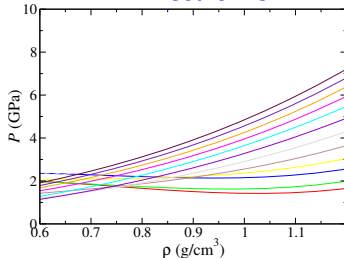
Limitations of Thermochemical Modeling

- Standard thermochemical tables are
 $T \sim 100's - 10000 \text{ K}$, $P \sim 0.01 - 150 \text{ GPa}$
- Limitations we understand:
 - predefined constituent catalog
 - potential form (mostly a problem for H_2)
 - equilibrium assumption
- Stuff we're less sure about:
 - $\mathcal{G} < 0$ at high pressures
 - $\Gamma < 0$ at high and low T

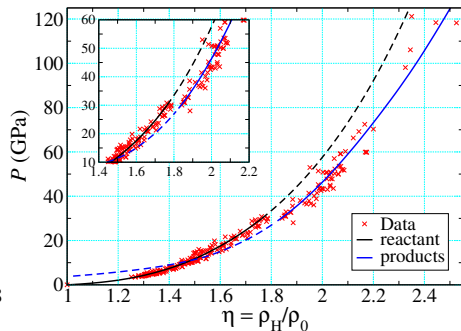
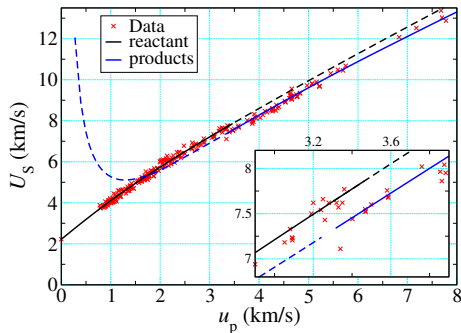
EXP6 potential



PMMA isotherms



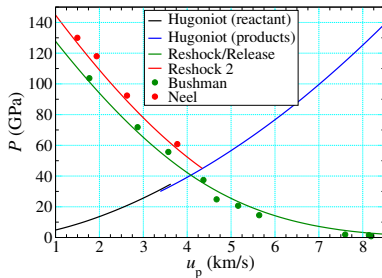
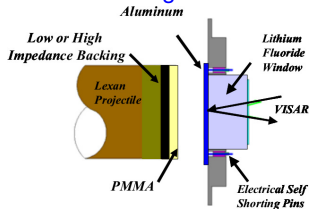
PMMA: Shock



- Dashed segments indicated metastability (reactant) or physical impossibility (products)
- E_{shift} from heat of combustion indistinguishable from optimized value

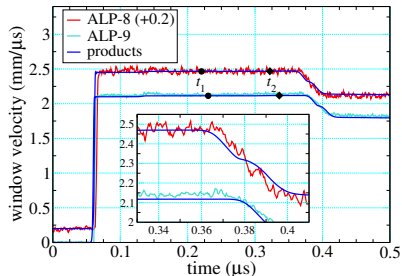
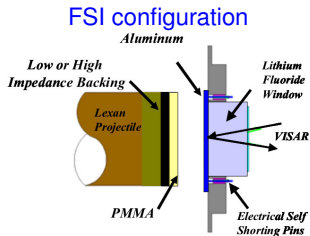
PMMA: Reshock and Release

FSI configuration

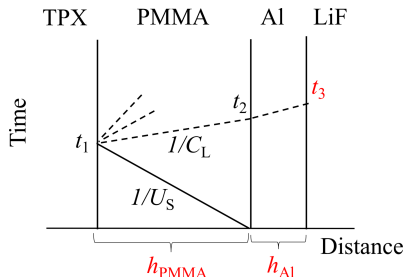


- SNL and Russian reshock/release experiments from common origin
 - SNL: $P \approx 45$ GPa
 - Russian: $P \approx 41$ GPa

PMMA: Sounds Speeds at Pressure



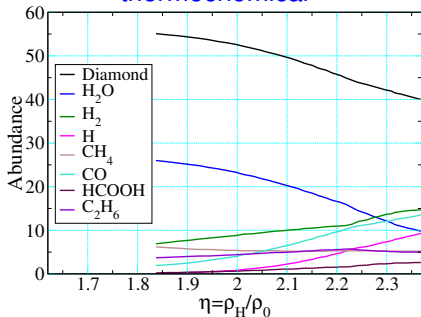
- t_3 is the observable, indicated by end of flat-top
- Metric is $\delta t_3 / (t_2 - t_1)$
- Errors in C_L of $< 5\%$
 - very similar results in PE



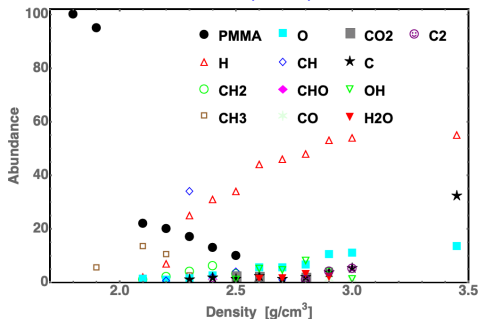
AIP Conf. Proc. **85**, 131 (2006); **1426**, 771 (2012)

PMMA: Product Compositions

thermochemical



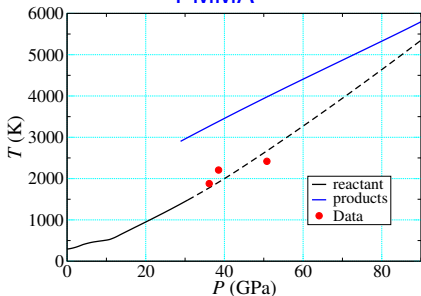
QMD (SNL)



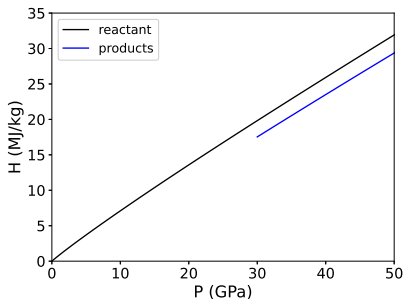
- Thermochemical products dominated by solid carbon and water
- Dominant change along the Hugoniot: $C + H_2O \rightarrow CO + H_2$
- Thermochemical can't see reactant (no time), QMD can't see phase segregation (system size and timescale limitations)
- Oversimplified vs. uncertain relation to thermodynamics

Product Temperatures & Reaction Thermicities

PMMA



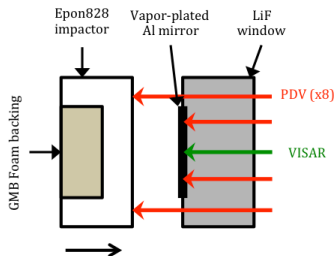
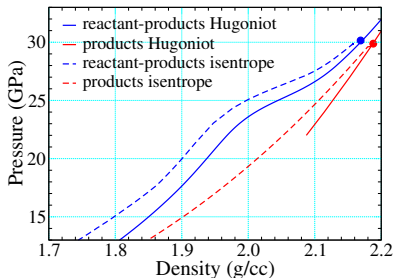
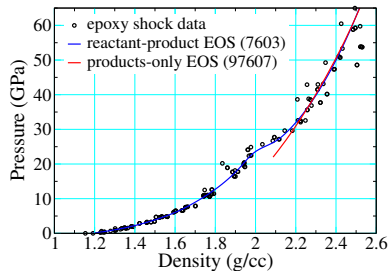
PMMA



- Thermochemical modeling consistently predicts large temperature rises
 - PMMA is only case in which we have actual data
 - Temperatures are most poorly constrained thermochemical quantity
- Reaction at constant pressure is exothermic

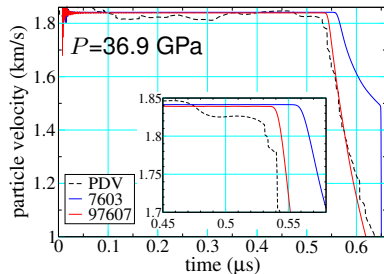
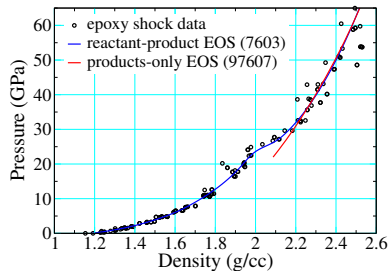
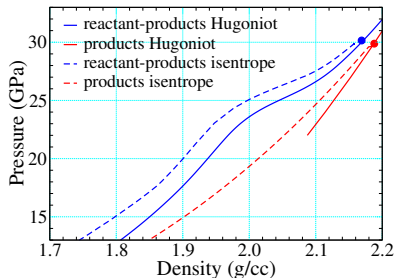
Old way of capturing “chemistry”

- Old EOS build structure into cold curve
- structure preserved in all isotherms until “washed out” by thermals



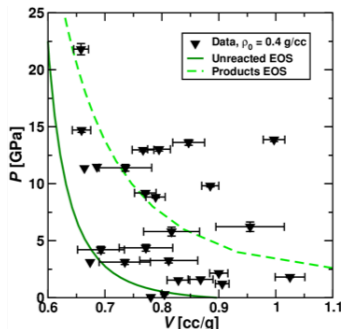
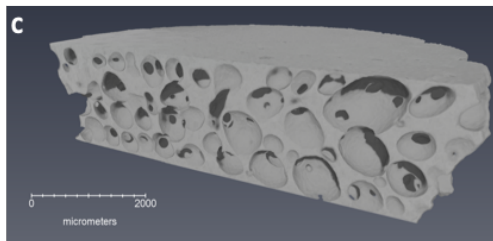
Old way of capturing “chemistry”

- Old EOS build structure into cold curve
- structure preserved in all isotherms until “washed out” by thermals
- produces multiwave structure upon release
- reversible phase transition rather than irreversible chemistry
- When might we care?



Heterogeneous Materials are Horrible People

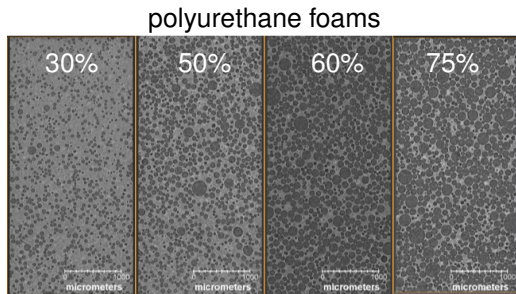
SX358



- Not always clear what you're probing
 - Spot size of our standard PDV is roughly $450 \mu\text{m}$
 - Pore diameters span range $\mathcal{O}(10 \mu\text{m} - 1 \text{ mm})$
- $U_S \approx u_p$, so $\sigma(\rho)$ large
- Shot-to-shot variability $>$ known sources of uncertainty
- We have the same problem with powders

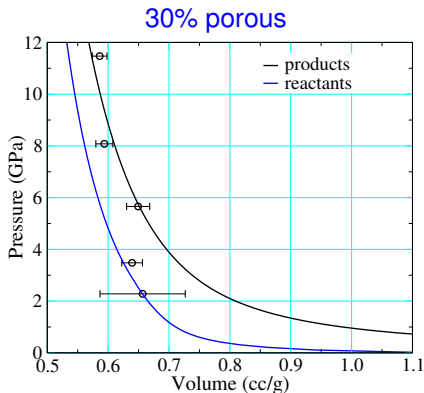
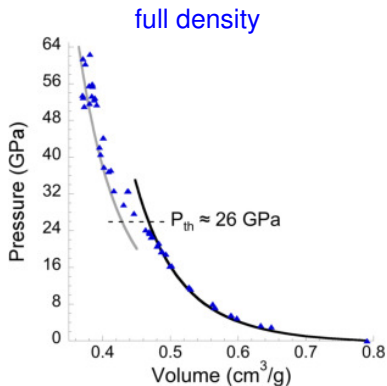
Image courtesy of Brian Patterson (MST-7, LANL), data courtesy of John Lang (M-9, LANL)

Adjustments for Porosity



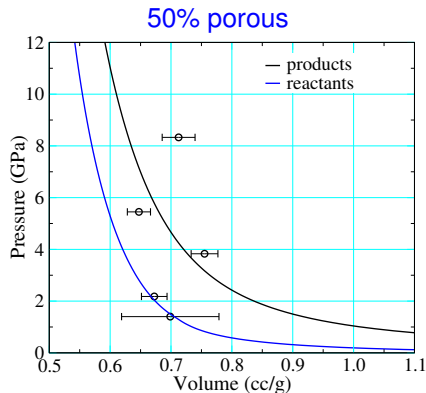
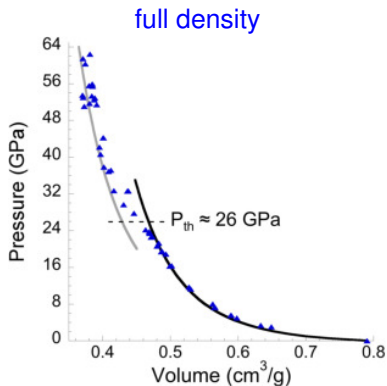
- Many polymers of interest to NNSA are porous, some highly
- Model reactant as SESAME + $P - \alpha$ porosity model
 - Only porous parameter is crush pressure, P_c
- Still thermochemical modeling for products
 - Vary E_{shift} as $f(\rho_0)$, if necessary

Polyurethane Results



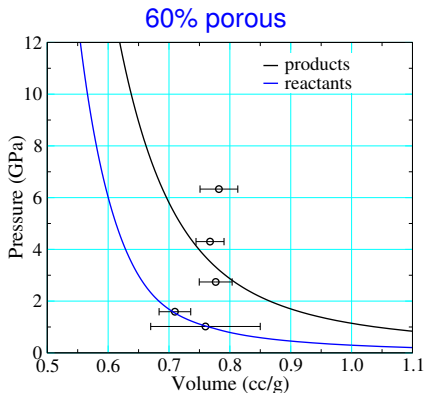
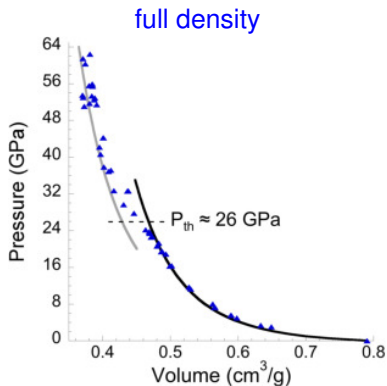
- Foam products expand relative to compressed reactant
- Reaction threshold drops dramatically as $f(\rho_0)$

Polyurethane Results



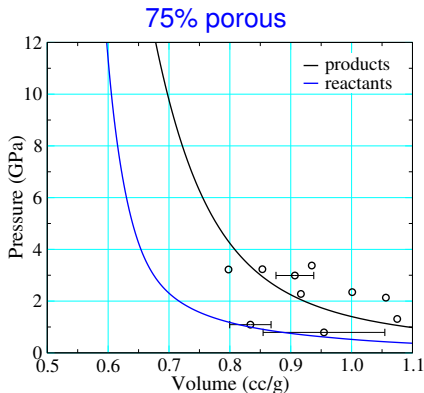
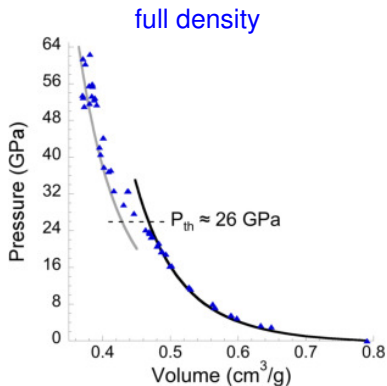
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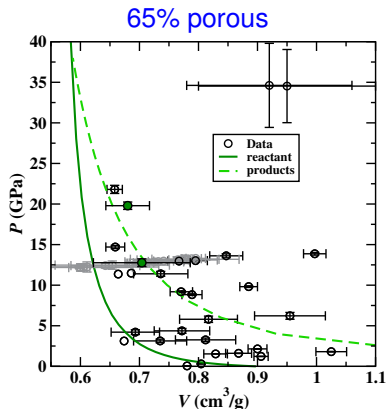
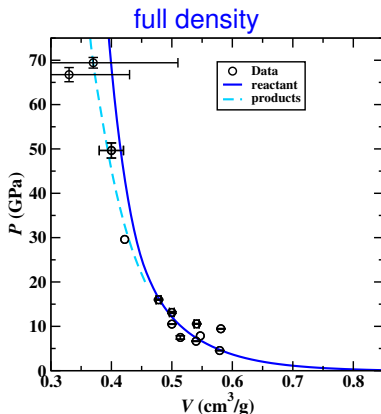
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Polyurethane Results



- Foam products expand relative to compressed reactant
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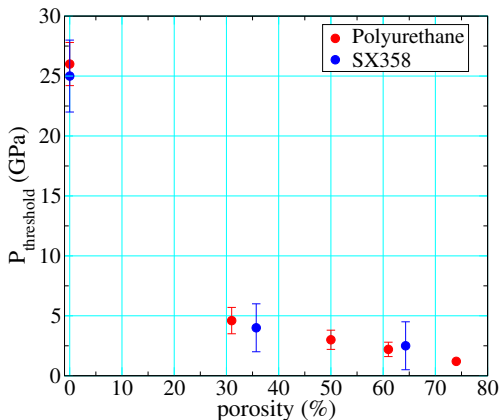
SX358 Results



- Patterns consistent with polyurethane
- Uncertainties again: multislug, multi-PDV

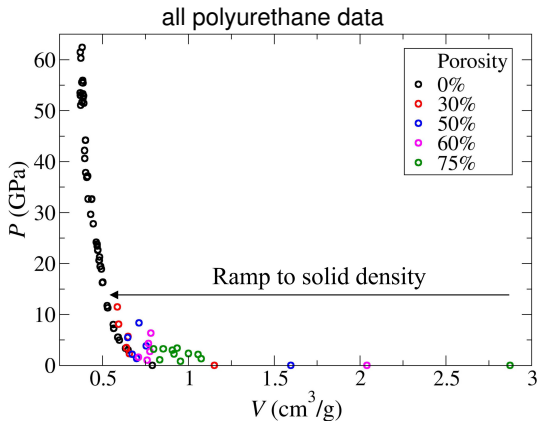
Data courtesy of John Lang (M-9, LANL); Brittany Branch and Chad McCoy (SNL); figure courtesy of Katie Maerzke (XTD-IDA, LANL)

Transition Thresholds



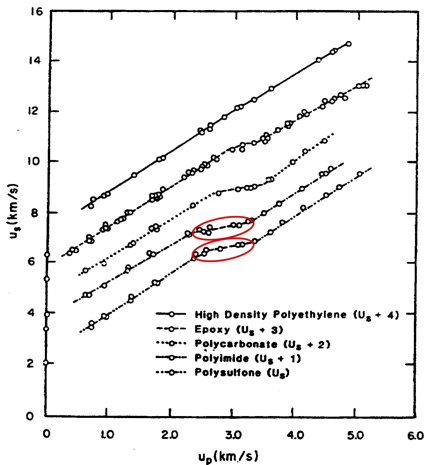
- Roughly exponential drop
- Strong dependence on timescale of experiment

Old Way of Treating Foams



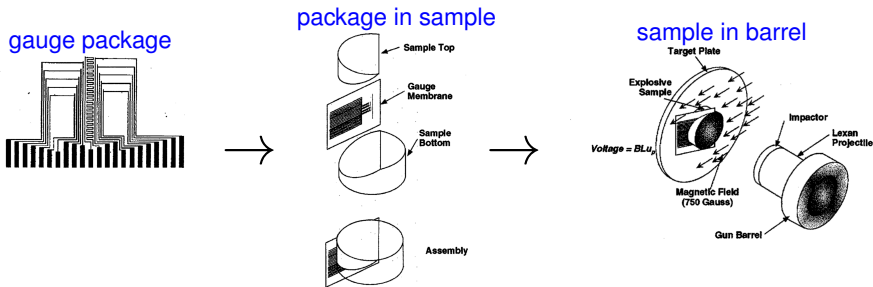
- Initialize at foam density, ramp to solid density Hugoniot
- Some error in density, energy, sound speed

Disentangling Non-Equilibrium Effects (or so we hoped)



- 1 embedded gauge, 5 transmission shots on polyimide
- similar series on polysulfone

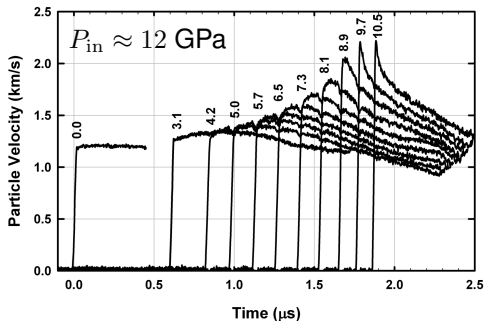
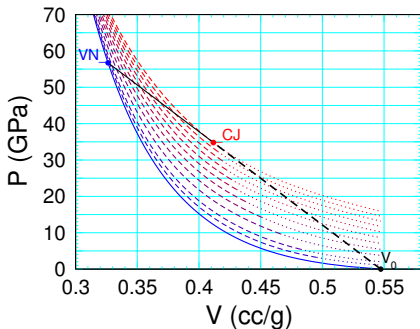
Measuring & Simulating Reactive Wave Evolution In Situ



- Embedded electromagnetic gauges
 - Advantage: minimizes measurement perturbation
 - Disadvantage: limited to insulating samples and impactors
- Hydrodynamic simulation requires:
 - Reactant and products EOS
 - Rate model. We used Arrhenius: $\mathcal{R} \equiv \dot{\lambda} = (1 - \lambda)^n \nu e^{-T_a/T}$
 - Closure rule. We used pressure-temperature equilibrium.

Sheffield, et al., 11th Int. Det. Symp. 451, (1998)

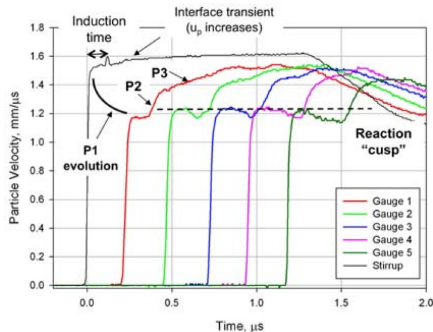
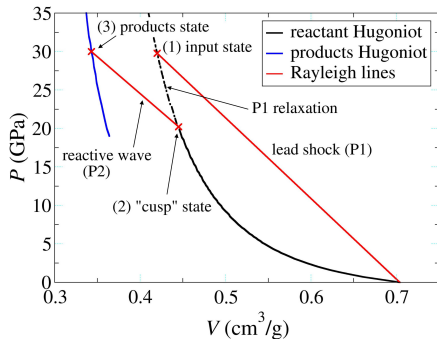
In Situ Wave Profiles: Energetic Materials



- ZND: inert shock followed by reaction zone to CJ state
- Reaction behind feeds the front, strengthening lead shock
- Reaction pushes unsteady \rightarrow steady

Menikoff, LA-UR-15-29498; Gustavsen, et al., *J. Appl. Phys.* **99**, 114907 (2006)

In Situ Wave Profiles: Phenylacetylene



- Reaction behind the front weakens lead shock
- Initial (P1) wave decays, second (P2) wave carries to products
- Decay and rise times contain kinetic information

Dattelbaum & Sheffield, *AIP Conf. Proc.* **1426**, 627 (2012); Sheffield thesis, WSU (1979)

Rate Model Calibration

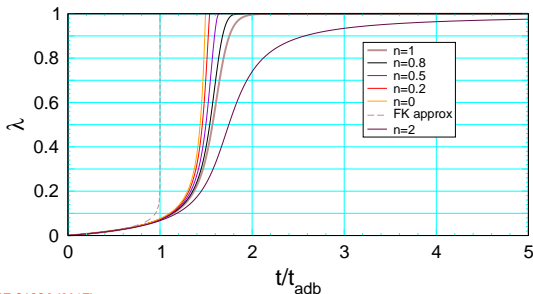
- We used $1/(\text{adiabatic induction time})$ as a proxy for the rate

$$t_{\text{ad}}(T_0) = \frac{T_0^2}{\nu T_a (T_1 - T_0)} e^{(T_a/T_0)}$$

T_0 = reactant temperature

T_1 = product temperature

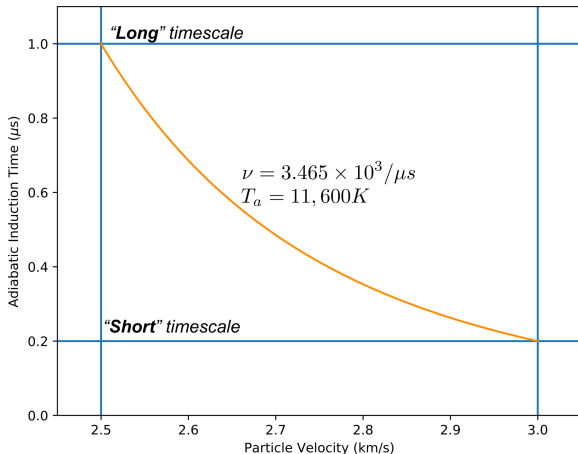
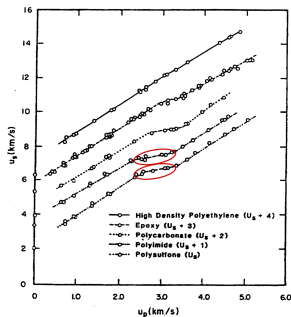
- In our case, these are Hugoniot temperatures



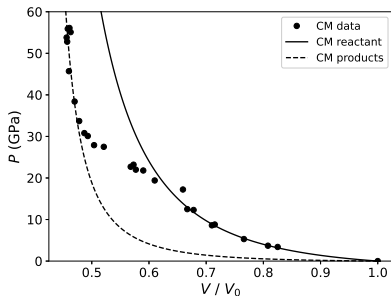
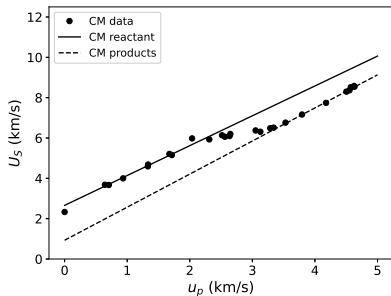
R. Menikoff, LA-UR-17-31024 (2017)

Rate Model Calibration

- Because $T_0 = T_0(u_p)$, we'll consider $t_{ad}(u_p)$
- For a given pair of EOS:
 - T_a sets u_p range
 - ν shifts laterally

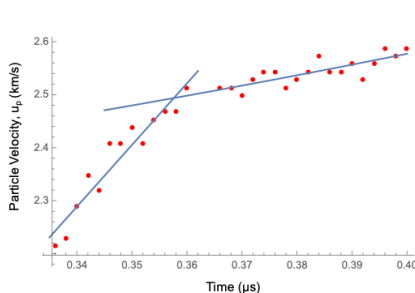
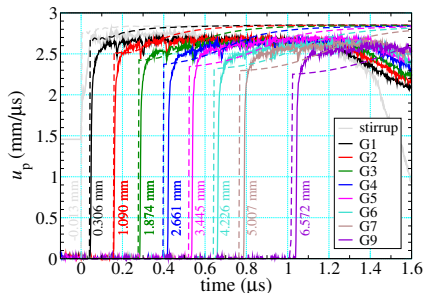


Polyimide Shock Data



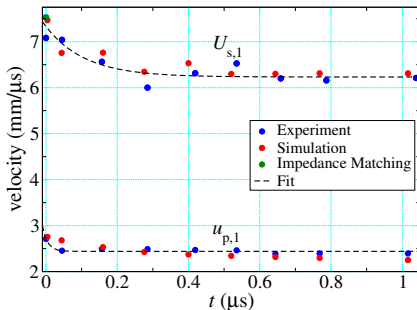
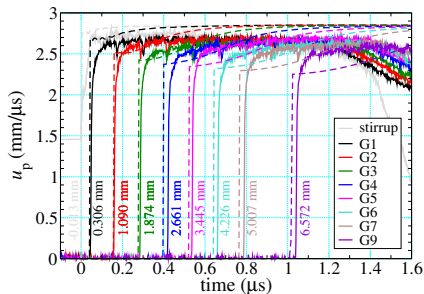
- CM reactant and products fits cross
 - Is this partly due to their including reacting points in their reactant fit?

Polyimide: Embedded Gauge Results



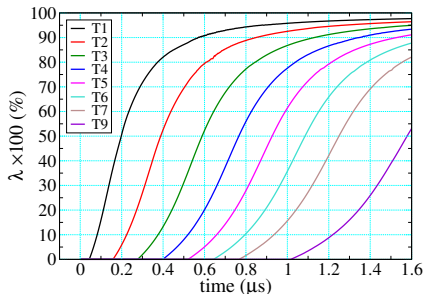
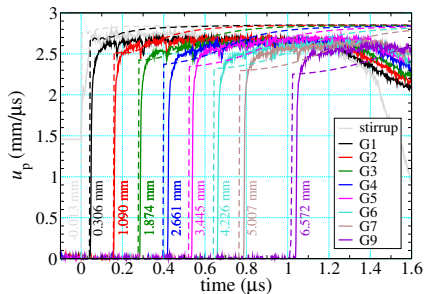
- Simulation: $50 \mu\text{s}$ (Eulerian) mesh, $Z = 830 \mu\text{s}^{-1}$, $T_a = 8560 \text{ K}$, $n = 2$
– Lagrangian tracers at gauge locations
- Experimental u_p analyzed similar to HE initiation data

Polyimide: Embedded Gauge Results



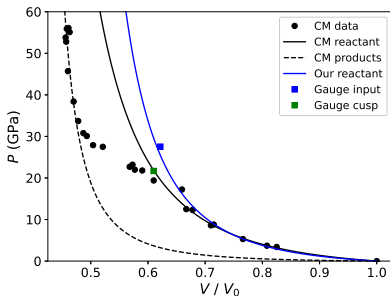
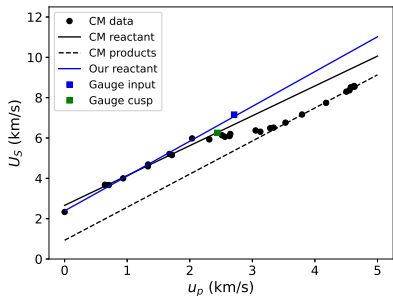
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Polyimide: Embedded Gauge Results



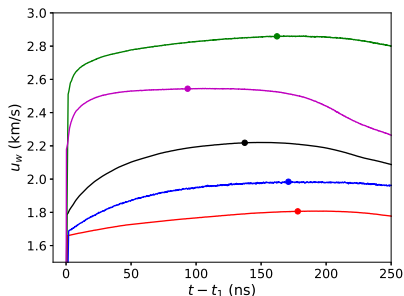
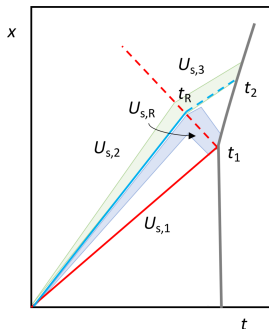
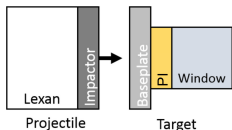
- Simulation: 50 μ s (Eulerian) mesh, $Z = 830 \mu\text{s}^{-1}$, $T_a = 8560 \text{ K}$, $n = 2$
 - Lagrangian tracers at gauge locations
- Experimental u_p analyzed similar to HE initiation data
- Attenuation of $\sim 15\%$ in both U_S and u_p , slightly large in simulation
- Data and simulations suggest sluggish reaction that doesn't proceed to completion
 \Rightarrow let's try a stronger input

Polyimide Shock Data



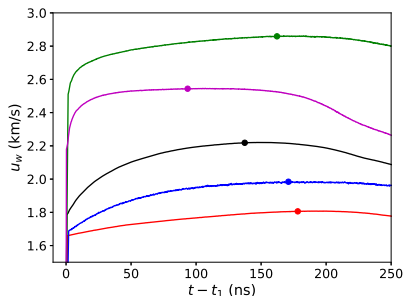
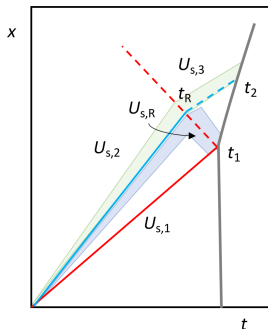
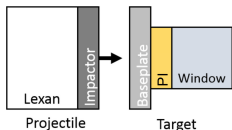
- CM reactant and products fits cross
 - Is this partly due to their including reacting points in their reactant fit?
- Gauge results:
 - Use input (blue square) to refit reactant (blue curve)
 - Reactant and products no longer cross
 - The cusp state (green square) lies on CM reactant (black line)
 - Does P1 relaxation have a long “tail”?

Polyimide Transmission Analysis



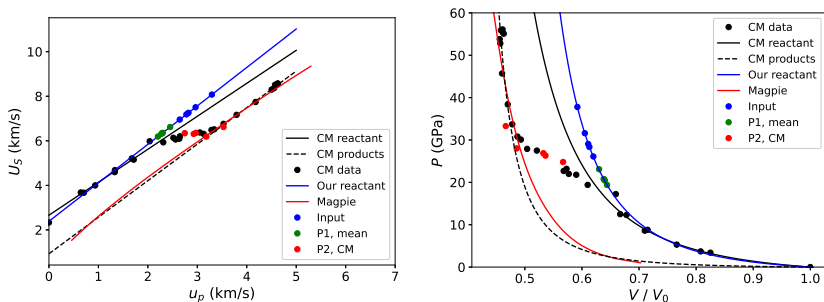
- Advantage: no restriction to non-conducting impactors
- Disadvantage: interaction with the window perturbs the flow
- The general problem is underdetermined – more unknowns than equations
 - Similar configurations: Wackerle (1962), Ahrens (1968), Erskine (1992), McWilliams (2008)
 - General theory: Courant & Friedrichs, Zel'dovich, Forbes

Polyimide Transmission Analysis



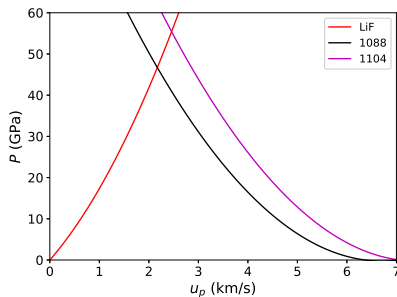
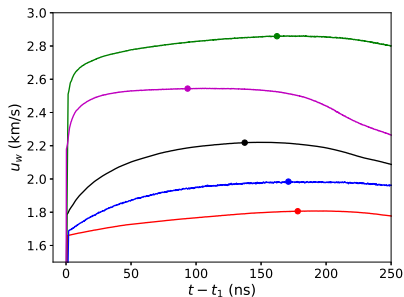
- Ignore wave-wave interaction \Rightarrow all about pinpointing t_2
- $P2$ is “thickened” (Zel’dovich) - what are the constraints on t_2 ?
 - $t_1 \leq t_2 \leq t(\max(u_w))$
 - $t_2 - t_1$ should decrease monotonically with P_{input}

Polyimide Transmission Analysis



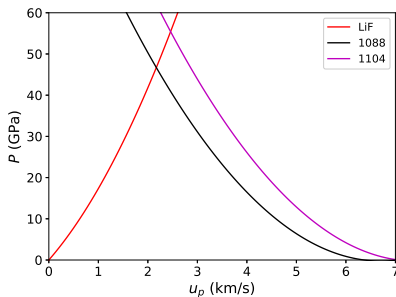
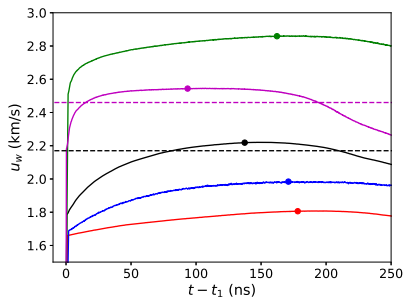
- Try the old way instead: $t_2 = t_1$ (red points)
 - Consistent with old results
 - 2 of 5 points appear fully reacted
 - So what is causing the structure in those profiles?

Polyimide Transmission Analysis



- Simplest reshock analysis: reflect old CM products fit and impedance match into LiF
 - Yields window velocities correct to within a few % (dashed, left panel)
- Reshocking one thickened wave yields...another thickened wave
 - Shift in composition from equilibrium shock to equilibrium reshock

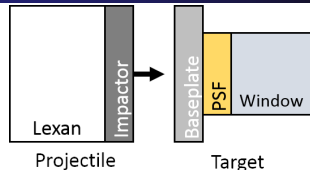
Polyimide Transmission Analysis



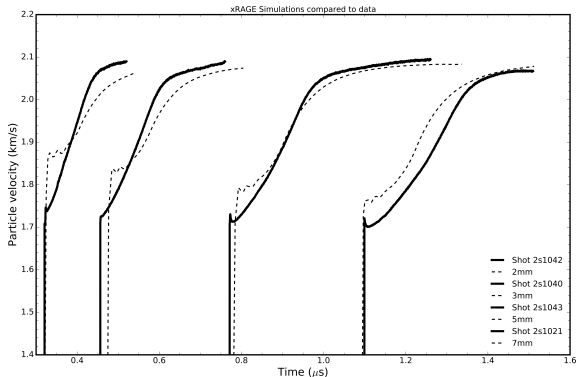
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Polysulfone Transmission Experiments

PDV at interface with window



increasing sample thickness →

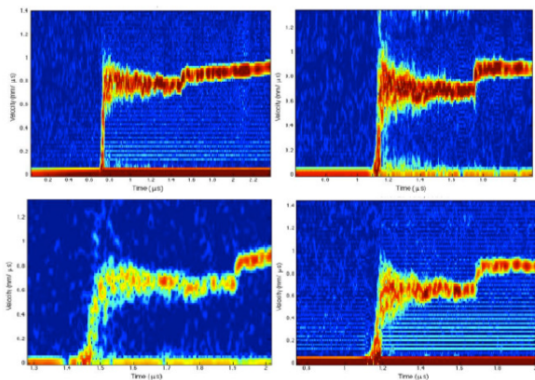


Simulation

- underestimates P1 decay
- exaggerates P1 variation with thickness
- P2 slow when thin, fast when thick

Reactive Wave Profiles: Foams

PDV in polyurethane foams



- Clockwise from upper left: 30%, 50%, 60%, 75% porous
- One wave observed
- PDV increasingly “bleached” due to high T

Summary

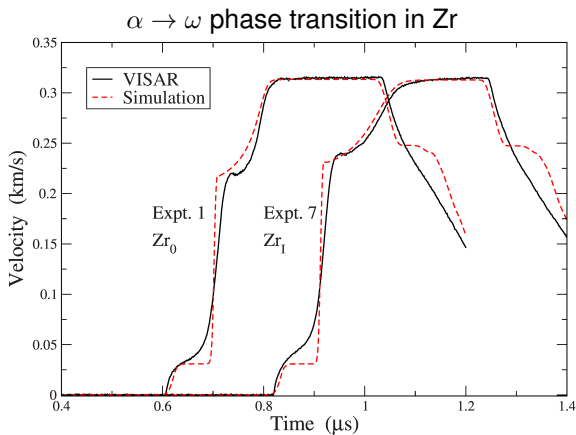
- Polymers decompose under shock loading
 - $u_p \sim 3$ km/s, $P \sim 25$ GPa at full density
 - This is not a reversible phase transition..
- Details affected strongly by porosity
 - Products expand upon reaction
 - Thresholds drop dramatically
- Polymer decomposition produces non-trivial wave evolution
 - Able to capture some qualitative features with simple rate model
 - Qualitative features of transmission profiles resemble those of metals
 - Unable to cleanly disentangle multiwave structure from interactions with window in transmission geometry

Acknowledgements, etc.

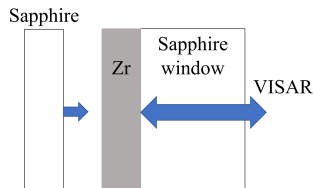
- LANL: Dana Dattelbaum, Tinka Gammel, Rachel Huber, John Lang, Jeff Leiding, Katie Maerzke, Jeff Peterson, Chris Ticknor, Kirill Velizhanin
- SNL: Brittany Branch, Kyle Cochrane, Patricia Kalita, Chad McCoy, Josh Townsend
- \$: Science Campaign 2, ASC PEM
- References
 - polyimide: in preparation, email jcoe@lanl.gov
 - pmma: *AIP Conf Proc* **2272**, 0700027 (2020), and in preparation
 - polysulfone: *JAP* **127**, 105902 (2020)
 - Mie-Grüneisen form: <https://arxiv.org/abs/2012.01169> (2020)
 - review: *Polymers* **11**, 493 (2019)
 - polyethylene: *JAP* **126**, 045902 (2019); *AIP Conf Proc* **1979**, 030004 (2018)
 - epoxy: *AIP Conf Proc* **1979**, 090008 (2018)
 - fiber-filled composites: *JAP* **116**, 194308 (2014)
 - polyurethane: *JAP* **115**, 174908 (2014)

Extra Slides

Transmission Profiles in Metals

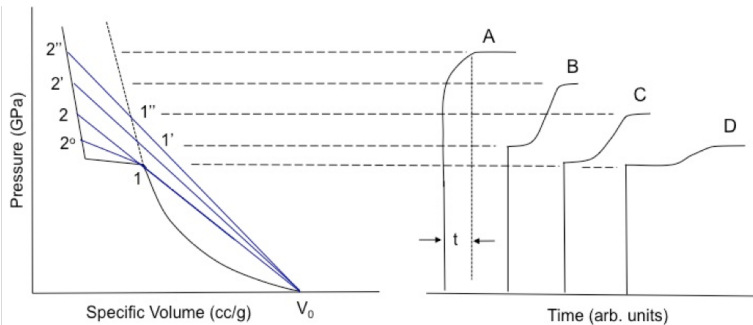


VISAR at (reshock)
interface with window



Rigg, et al., *J. Appl. Phys.* (2009)

Reactive Wave Profiles: Schematic



- Reaction behind weakens lead shock
- Waves separate rather than converge
- Initial (P1) wave decays, second (P2) wave carries to products
- Decay and rise times contain kinetic information

Dremin, Combust. Explos. Shock Waves (1965); Dattelbaum AIP Conf. Proc. (2018)

Detonation Criterion

- In order to produce a self-sustaining wave, a material must have a positive thermicity coefficient, σ :

$$\sigma = \left(\frac{\partial P}{\partial \lambda} \right)_{V,E} = \frac{\Delta V}{V} - \frac{\Gamma}{c^2} \Delta H$$

λ = reaction progress variable

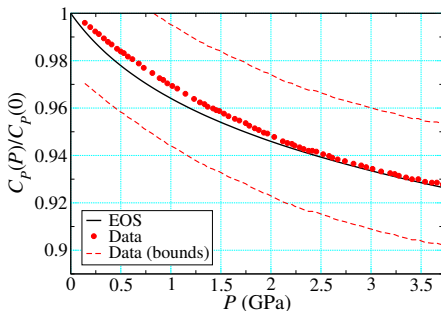
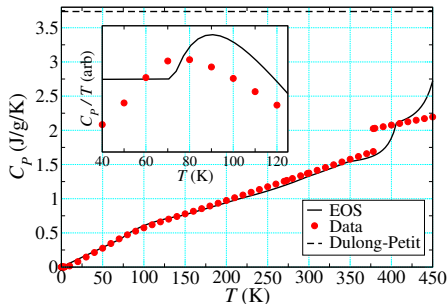
Γ = Grüneisen parameter

$c^2 = (\partial P / \partial \rho)_{S,\lambda}$ = frozen sound speed

$\Delta = (\partial / \partial \lambda)_{T,P}$

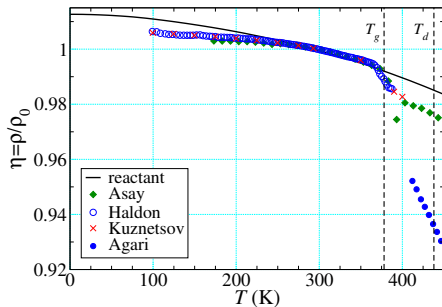
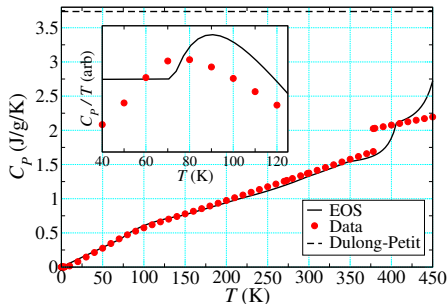
- Exothermicity ($\Delta H < 0$) isn't sufficient (or even necessary!) for detonation
 - “The importance of the volume term has often been overlooked...”

PMMA: Reactant Thermal



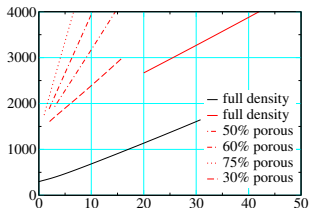
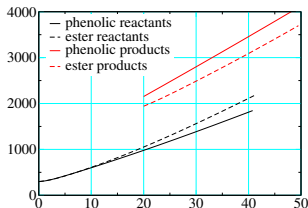
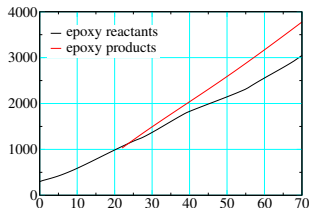
- $C_P \propto T$ at low T , never gets to classical limit
 - We shove glass transitions and decomposition into melt
- Expansion surprisingly good given M-G constraint

PMMA: Reactant Thermal



- $C_P \propto T$ at low T , never gets to classical limit
 - We shove glass transitions and decomposition into melt
- Expansion surprisingly good given M-G constraint

Temperature Usually Increases



- In most cases we find $T > 0$ upon decomposition
- Foam temperatures very high due to $P - V$ work
- High T observable in “bleached” PDV signal

Dattelbaum and Coe, *Polymers* (2019)